Mass Spectral Fragmentation Pattern of 3-Methyl-4-arylaminomethyleneisoxazol-5-ones

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The mass spectral fragmentation patterns of 3-methyl-4-arylaminomethyleneisoxazol-5-ones obtained by electron impact have been elucidated. The base peaks are due to the molecular ions. The main fragmentation routes involve loss of H, OH, H_2O, CO_2 and COOH from the molecular ions as well as rupture of the exocyclic CH-NH bond.

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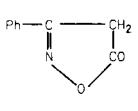
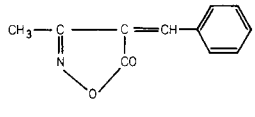
There has been much interest in the electron impact mass spectra of isoxazoles and isoxazolones over the past decade. In the initial studies it was found that the dominant fragmentation route from the molecular ion of 3,5-dimethylisoxazole involved rupture of the N-O bond followed by rearrangement of the molecule (1). Similar processes occurred with 3,5-diphenylisoxazole (2). In both cases the base peak was not due to the molecular ion. Considerable further work (3-21) with a variety of isoxazoles has confirmed that fission of the N-O bond and subsequent rearrangements commonly take place. With isoxazolones, fragmentation routes other than those involving splitting of the N-O bond with concomitant rearrangements can sometimes predominate. In 3-phenylisoxazol-5-one (I), for example, the base peak is due to a species of mass 103 (C_8H_7) due to loss of N-O-CO from the molecular ion (1), (21), (22), while with 3-methyl-4-benzylideneisoxazol-5-one (II) (see also ref. 23) the base peak is at mass 128 ($C_{10}H_8$) due to the loss of N-O-CO plus H from the molecular ion (1). Other peaks due to species not involving rupture of the N-O bond are also present in the spectrum of (I). In the mass spectra of 3-methyl-4-arylhydrazonoisoxazol-5-ones (III) fragmentation is initiated both by cleavage of the heterocyclic ring and by the exocyclic arylhydrazono moiety (24). The mass spectra of 5-alkylisoxazol-3-ones (*e.g.* IV) which involve several basic fragmentation routes have also been reported (25). This paper is concerned with the electron impact mass spectra of 3-methyl-4-phenylaminomethyleneisoxazol-5-one (V, R = H) and the three 3-methyl-4-tolylaminomethyleneisoxazol-5-ones (V, R = CH_3). These compounds have been shown to exist as structure (V) with hydrogen bonding between the CO and NH groups and not as other possible tautomeric forms both in solution and in the solid state (26).



I



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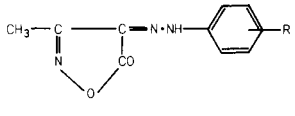

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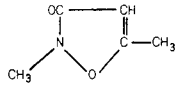

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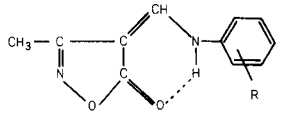
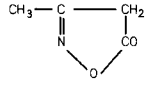


V



VI

Unlike 3-methylisoxazol-5-one (VI) (21), 3-phenylisoxazol-5-one (I) (1) (21) (22), 3-methyl-4-benzylideneisoxazol-5-one (II) (1) and 3-methyl-4-phenylhydrazonoisoxazol-5-ones (III) (24), the base peaks in the mass spectra of the four 3-methyl-4-arylaminomethyleneisoxazol-5-ones (Figures 1-4) are all due to the molecular ions. There are several competing fragmentation routes from the molecular ion. These will be dealt with in turn.

Loss of $H^{\cdot}$ to form the M-1 ion occurs with 3-methyl-4-phenylaminomethyleneisoxazol-5-one (V, R = H). This gives rise to a peak of 9% of the intensity of the base peak. The species responsible for the M-1 peak is depicted as an isoxazoloisoxazole derivative. These species may be formed by loss of the hydrogen associated with the hydrogen bonding in (V, R = H). The three tolylamino derivatives behave similarly. In keeping with this structural assignment for the M-1 ion it fragments to a small extent by loss of the elements $CH_3{\cdot}CNO$ to form a $C_9H_6NO^+$ ion at mass 144 (4%) as shown in Scheme 1. A strong metastable was observed for the transition 201 → 144. The three tolyl

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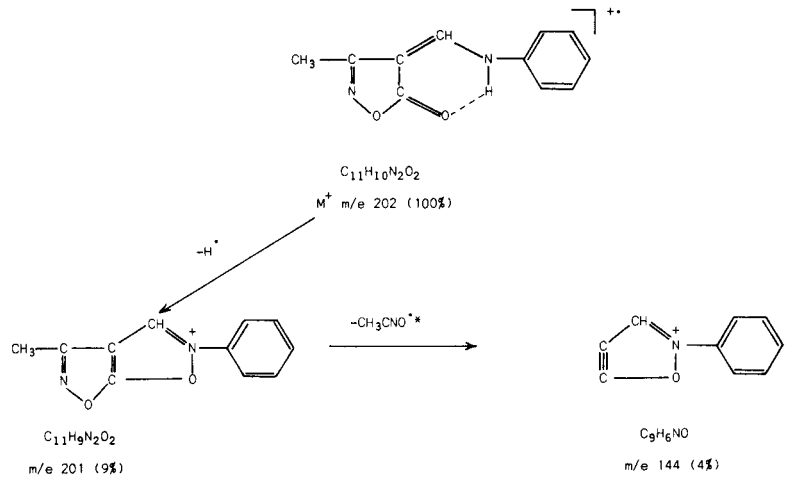
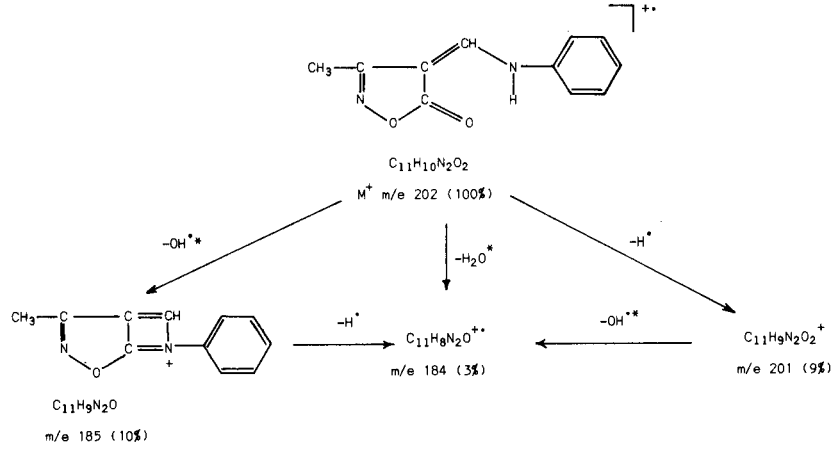


SCHEME 1



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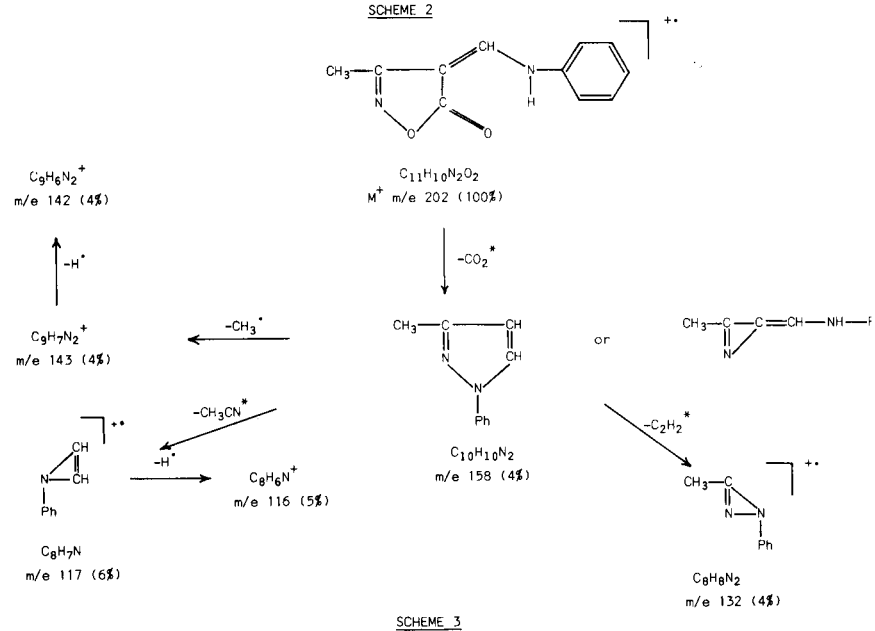


SCHEME 3

Table 1

Empirical Formula of Fragment Ions (a) in the Mass Spectra of 3-Methyl-4-arylaminomethyleneisoxazol-5-ones (V)

m/e	Formula	Intensity [%]			
		R = H	R = 2-CH_3	R = 3-CH_3	R = 4-CH_3
216	$C_{12}H_{12}N_2O_2$	—	100	100	100
215	$C_{12}H_{11}N_2O_2$	—	9	12	15
202	$C_{11}H_{10}N_2O_2$	100	—	—	—
201	$C_{11}H_9N_2O_2$	9	1	—	—
199	$C_{12}H_{11}N_2O$	—	1	7	11
198	$C_{12}H_{10}N_2O$	—	—	2	3
185	$C_{11}H_9N_2O$	10	—	—	—
184	$C_{11}H_8N_2O$	3	—	—	—
174	$C_{10}H_8NO_2$	—	3	—	1
173	$C_{10}H_9N_2O$	—	3	—	2
	$C_{11}H_{11}NO$	—	1	—	—
172	$C_{11}H_{12}N_2$	—	—	3	—
	$C_{11}H_{10}NO$	—	2	—	—
171	$C_{11}H_{11}N_2$	—	16	12	12
170	$C_{11}H_{10}N_2$	—	2	1	2
169	$C_{11}H_9N_2$	—	1	—	1
159	$C_{10}H_{11}N_2$	—	1	1	1
158	$C_{10}H_{10}N_2$	4	—	1	—
	$C_{10}H_8NO$	—	2	2	2
157	$C_{11}H_{11}N$	—	2	—	1
	$C_{10}H_9N_2$	18	9	3	4
	$C_{10}H_7NO$	—	5	1	—
156	$C_{11}H_{10}N$	—	4	1	1
	$C_{10}H_8N_2$	2	6	3	4
	$C_{10}H_6NO$	—	2	1	—
155	$C_{11}H_9N$	—	3	1	—
	$C_{10}H_7N_2$	1	4	2	3
154	$C_{11}H_8N$	—	2	—	—
146	$C_9H_{10}N_2$	—	6	5	3
	C_9H_8NO	—	1	—	—
145	$C_9H_9N_2$	—	6	8	6
144	$C_{10}H_{10}N$	—	4	3	4
	C_9H_6NO	4	—	—	—
143	$C_{10}H_9N$	—	4	2	2
	$C_9H_7N_2$	4	—	—	—
	C_9H_5NO	2	—	—	—
142	$C_{10}H_8N$	2	4	2	2
	$C_9H_6N_2$	6	3	2	2
141	$C_{10}H_7N$	1	1	—	—
135	C_8H_9NO	—	—	2	3
132	$C_9H_{10}N$	—	2	2	2
	$C_8H_8N_2$	4	—	—	—
131	C_9H_9N	—	4	2	3
	$C_8H_7N_2$	6	7	2	3
130	C_9H_8N	3	18	8	6
129	$C_{10}H_9$	—	—	1	1
	C_9H_7N	2	4	2	2
128	$C_{10}H_8$	—	—	2	2
	C_9H_6N	2	4	1	2
119	$C_7H_7N_2$	—	—	3	2
	C_7H_5NO	2	—	—	—
118	C_8H_6N	3	21	9	6
117	C_8H_7N	6	5	1	2
116	C_8H_6N	5	2	1	2
115	C_9H_7	3	2	1	2
	C_8H_5N	2	2	—	—

Table 1 Continued

m/e	Formula	Intensity [%] R = H	R = 2-CH_3	R = 3-CH_3	R = 4-CH_3
110	$C_6H_6O_2$	—	1	2	—
	$C_5H_4NO_2$	22	15	4	7
109	$C_5H_5N_2O$	2	2	—	—
108	C_7H_8O	—	2	2	3
	C_6H_6NO	—	1	5	3
107	C_7H_9N	—	14	10	12
	C_7H_7O	—	1	1	—
106	C_7H_8N	—	10	6	8
105	C_8H_9	—	—	—	2
	C_7H_7N	2	1	—	1
	$C_6H_5N_2$	6	—	1	—
104	C_8H_8	—	—	—	2
	C_7H_6N	12	2	2	1
103	C_8H_7	1	4	3	4
102	C_8H_6	1	2	1	1
101	C_8H_5	4	1	1	4
93	C_6H_7N	18	—	1	1
92	C_7H_8	—	—	2	4
	C_6H_6N	2	—	—	—
91	C_7H_7	3	18	24	22
	C_6H_5N	2	—	—	—
90	C_7H_6	5	3	3	2
89	C_7H_5	5	4	4	4
82	C_4H_4NO	4	6	3	3
	$C_4H_2O_2$	8	—	—	—

(a) Only those ions of mass > 80 and of intensity ≥ 1% of the base peak are recorded. Peaks due to ^{13}C species are omitted from the table.

derivatives also lose $CH_3{\cdot}CNO$ from the M-1 ions to give analogous species which give rise to peaks of 1-2% of the base peak.

One major fragmentation route from the molecular ion of (V, R = H) involves the loss of $OH^{\cdot}$ to form a $C_{11}H_9N_2O^+$ ion at mass 185 (10%). The $C_{11}H_9N_2O^+$ ion is depicted as an azetoisoxazole derivative (Scheme 2). A strong metastable for the transition 202 → 185 is observed in the spectrum. The $C_{11}H_9N_2O^+$ ion may lose $H^{\cdot}$ to form a $C_{11}H_8N_2O^{+\cdot}$ species at mass 184 (3%). The $C_{11}H_8N_2O^{+\cdot}$ species is also formed from the molecular ion by loss of H_2O, for which transition a metastable is observed, and from the M-1 ion by loss of $OH^{\cdot}$. The *m*-tolyl and *p*-tolyl derivatives behave in the same way but with the *o*-tolyl derivative the M-OH species gives a peak of only 1% of the base peak while the M-H_2O species is not observed at all in the spectrum. Perhaps steric factors account for this difference.

Another fragmentation pathway from the molecular ion of (V, R = H) involves the loss of CO_2 to afford a $C_{10}H_{10}N_2^{+\cdot}$ species at mass 158 (4%). A metastable for the transition 202 → 158 is present in the spectrum. The $C_{10}H_{10}N_2^{+\cdot}$ species is depicted either as a pyrazole or an aziridine derivative (Scheme 3). This species may lose $CH_3^{\cdot}$ to afford a $C_9H_7N_2^+$ ion at mass 143 (4%), CH_3CN to afford a $C_8H_7N^{+\cdot}$ species at mass 117 (6%) or C_2H_2 to afford $C_8H_8N_2^+$ ion at mass 132 (4%). Metastable peaks for the transitions 158 → 117 and 158 → 132 are observed in the spectrum. The loss of CO_2 is observed from the molecular ion of the *m*-tolyl analogue but not from the *o*-tolyl or *p*-tolyl derivatives. However, peaks due to the loss of $CO_2 + CH_3$, $CO_2 + C_2H_2$ and $CO_2 + CH_3CN$ are observed in the spectra of all three tolyl derivatives.

A major fragmentation route from the molecular ion of (V, R = H) involves loss of $COOH^{\cdot}$ to afford a $C_{10}H_9N_2^+$ ion at mass 157 (18%). This ion is also formed from the M-1 ion by loss of CO_2 and presumably also by loss of $H^{\cdot}$ from the $C_{10}H_{10}N_2^{+\cdot}$ species just discussed. The structure of the $C_{10}H_9N_2^+$ ion is not clear but it is depicted as an aziridine, pyrazole or pyridazine derivative (Scheme 4). It loses HCN to afford a $C_9H_8N^+$ ion at mass 130 (3%) or C_2H_2 to afford a $C_8H_7N_2^+$ ion at mass 131 (6%). Metastables for the transitions 157 → 130 and 157 → 131 are observed in the spectrum. The three tolyl derivatives disintegrate in a corresponding way.

As well as these fragmentation routes the molecular ion of (V, R = H) also fragments at the exocyclic CH-NH bond. The straightforward bond rupture to form the $C_5H_4NO_2^+$ ion at mass 110 (22%) and the $C_6H_6N^+$ ion at mass 92 (2%) occurs to a large extent. The exocyclic bond rupture may also be accompanied by a hydrogen migra-

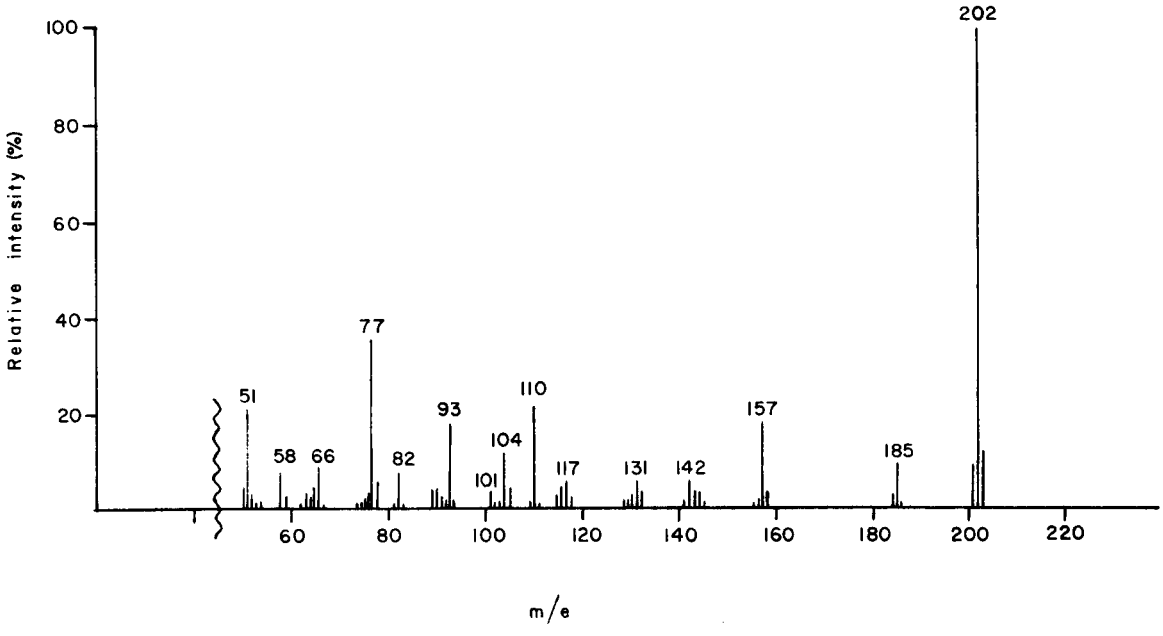


Figure 1: Mass spectrum of 3-methyl-4-phenylaminomethyleneisoxazol-5-one (V, R = H).

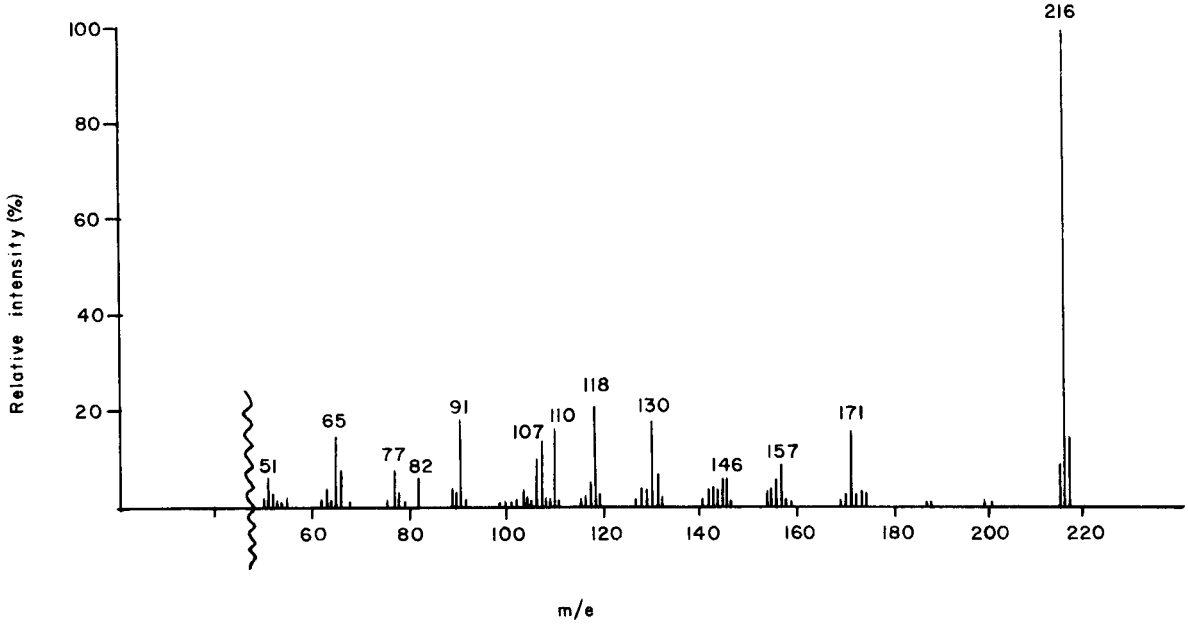


Figure 2: Mass spectrum of 3-methyl-4-*o*-tolylaminomethyleneisoxazol-5-one (V, R = 2-CH_3).

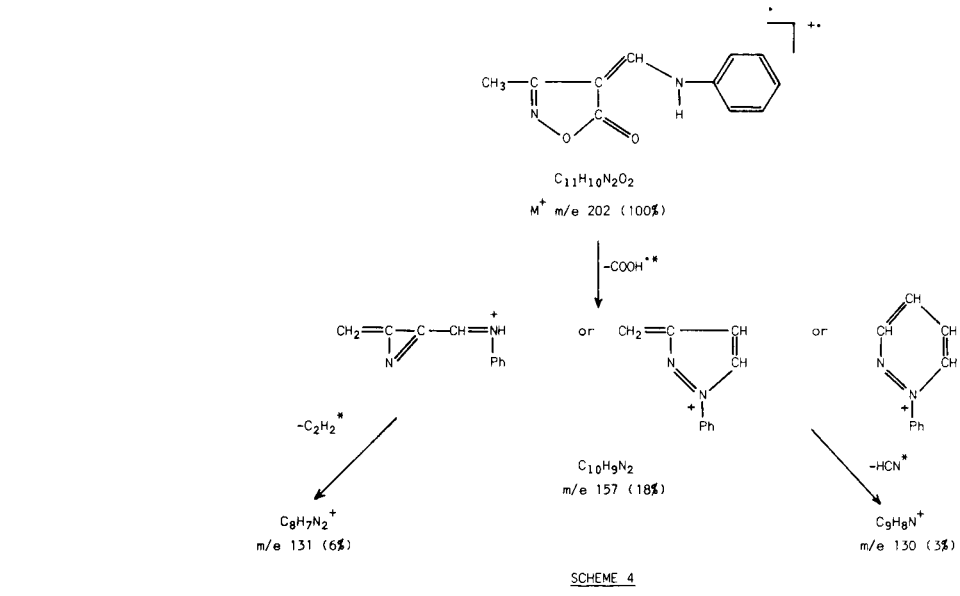
tion as evidenced by the presence of the $C_6H_7N^{+\cdot}$ species at mass 93 (18%). The accompanying fragment, the $C_5H_3NO_2^{+\cdot}$ species at mass 91 survives only in very small amounts (<1%). The three tolyl derivatives behave in an analogous way.

The empirical formulae of the fragment ions are given in Table 1.

EXPERIMENTAL

The spectra were determined with an A.E.I. MS-30 mass spectrometer. The samples were analysed by a direct insertion probe at an ionising current of 70 eV. The ion source temperature was 100°C. Elemental compositions were obtained by the peak matching method.

3-Methyl-4-phenylaminomethyleneisoxazol-5-one (V, R = H) and the three tolylamino analogues (V, R = 2-CH_3), (V, R = 3-CH_3) and (V, R = 4-CH_3) were analytically pure (26).



SCHEME 4

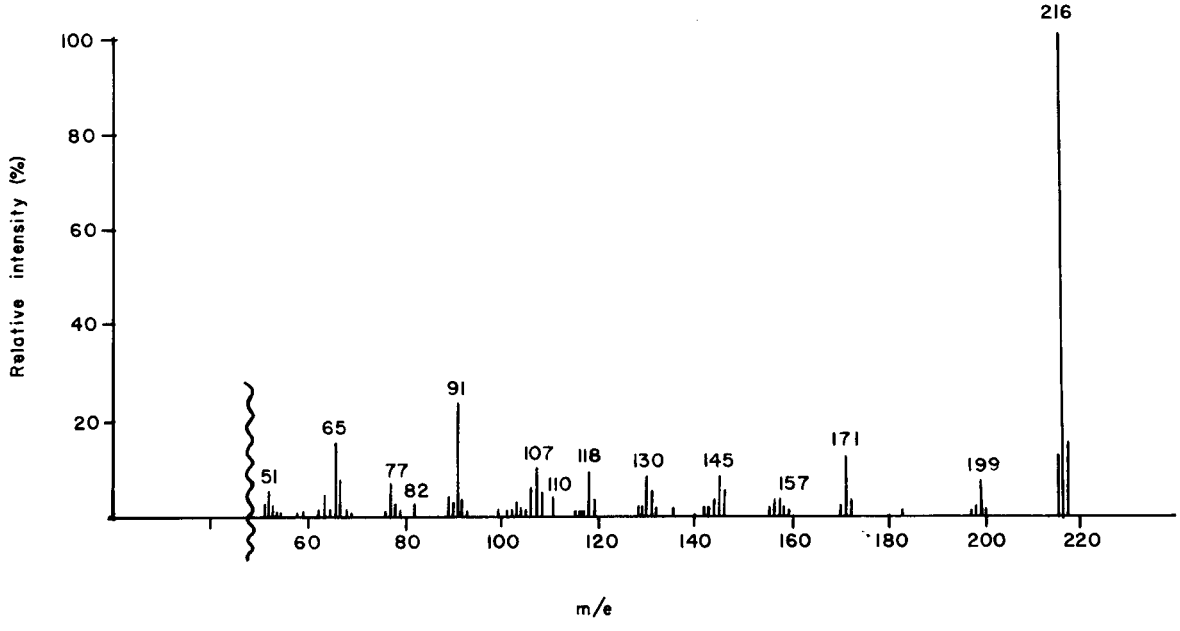


Figure 3: Mass spectrum of 3-methyl-4-*m*-tolylaminomethyleneisoxazol-5-one (V, R = 3-CH_3).

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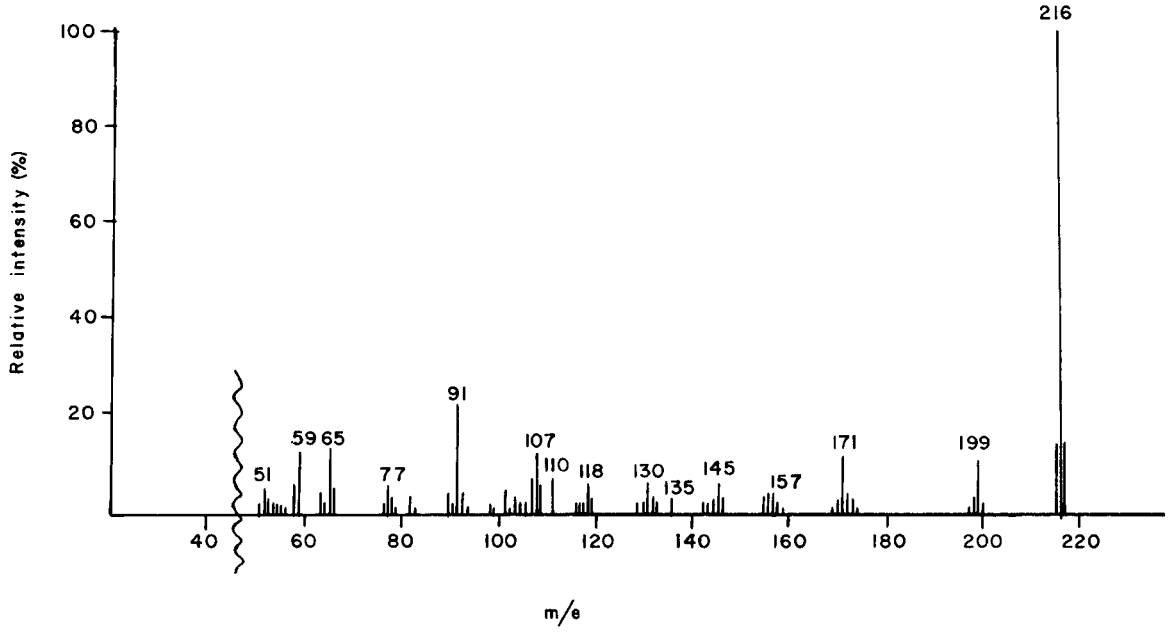

Figure 4: Mass spectrum of 3-methyl-4-*p*-tolylaminomethyleneisoxazol-5-one (V, R = 4-CH_3).

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